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FOGGING-FREE ADHESIVE TAPE

[Die folgenden Angaben sind den vom Anmelder eingereichten Unterlangen entnommen]

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Description /2*

The invention concerns a fogging-free adhesive tape and its use.

The test according to DIN 75 201 is used to determine the fogging behavior of active substances, which are used in the passenger space of motor vehicles. The fogging behavior of liquid, pasty, powdery, and solid raw materials, of which the work materials

consist or are produced can also be determined with this process.

Fogging accordingly describes the condensation of evaporated volatile components from the motor vehicle interior trim on the glass panes, in particular, on the windshield. With unfavorable illumination conditions, the fogging precipitate can impair viewing through the windshield.

In accordance with DIN 75 201, the fogging value F is the quotient, in percent, of the 60° reflectometer value of a glass plate with a fogging precipitate and the 60° reflectometer value of the same glass plate without a fogging precipitate.

The condensable component G is the difference of the weights of an aluminum foil with and without a fogging precipitate.

The methods which are used for the measurement of the fogging value will be described briefly in the following.

Method A

The specimen or the sample is brought onto the bottom of a glass beaker, without a spout (in the text below, referred to as beaker) and with fixed dimensions.

The beaker is covered with a glass plate on which volatile components from the specimen or the sample can condense. This glass plate is cooled.

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* [Numbers in right margin indicate pagination of the original text.]

The beaker thus prepared is placed, for three hours, in a bath thermostat, which is at a test temperature of (100 +/- 0.3)°C.

The effect of the fogging precipitate on the glass plate is determined by the measurement of the 60° reflectometer values. The 60° reflectometer values of the same glass plate without a precipitate, which was carefully cleaned before the experiment, was thereby used as a reference.

Method B

The specimen or the sample is placed on the bottom of a glass beaker, without a spout (in the text below, referred to as a beaker) and with fixed dimensions. The beaker is covered with aluminum foil, on which volatile components from the specimen or the sample can condense. This aluminum foil is cooled.

The beaker thus prepared is placed in a bath thermostat for 16 h, which is at the test temperature of (100 +/- 0.3)°C.

The weight of the fogging precipitate on the aluminum foil is quantitatively determined by weighing the film before and after the fogging experiment.

The exact carrying out of the experiments, along with the test apparatuses to be used, is described, in detail, in DIN 75 201. The contents of this norm should therefore be considered part of the disclosure of this application.

The determination of the fogging method is becoming increasingly important in the motor vehicle industry since as a result of ecological considerations, customers more and more frequently want raw materials in their car which do not represent hazards to human health.

Such statements can also be utilized very well in marketing techniques.

Also, there are many test methods for the determination of fogging behavior in the motor vehicle industry. All test methods are thereby stipulated in internal plant norms, which are based, more or less,

on DIN 75 201. Thus, in accordance with the Volkswagen AG Central Norm PV 3015, 55 11 6 "Nonmetal materials of the inside trim; Determination of condensable components (G)," first publication, March 1989, the determination of the fogging condensation product value of materials of the motor vehicle inside trim takes place, in that the condensable component is determined as the difference of the weights of an aluminum foil with and without fogging precipitate. Then, according to the "Corporate Standard" STD 1027, 2711, published in August 1994, Volvo determines the fogging value by comparing a clean glass pane (degree of light permeability 100%) with a pane covered by fogged-out material (degree of light permeability less than 100%). Moreover, the "Ford Laboratory Test Method" (BO 116-03), published on May 14, 1990, is known, which also measures the fogged-out precipitate of an experimental body on a pane. All mentioned documents, accessible to the public, should also be comprised by the disclosure of this invention.

The area of a motor vehicle to be tested with respect to the fogging behavior has self-adhesive tapes, which, for example, are used to wrap around cable harnesses.

In the cable bundle industry, the use of self-adhesive tapes is widespread. Depending on the requirements and usage area, articles are used with fabrics, nonwovens, or foils made of different materials. The coating of these carriers with pressure-sensitive, self-adhesive compositions is known. In accordance with experience, both solvent compositions and hot-melt compositions based on synthetic or natural rubber, with adhesive resins and perhaps fillers, are used here.

This type of adhesive tape is incorporated into all areas of the automobile (for example, the space for the engine, or the interior space).

A disadvantage which affects all the known articles is the evaporation of volatile components with heating. This process produces a coating on the window pane in the interior space of automobiles, so that the viewing impairment is classified as a safety risk. This evaporation process is, as indicated already /3

above, called "fogging" in the automobile industry.

Furthermore, double-sided adhesive tapes, based on acrylate adhesive compositions, have been known for a long time. For products with a balanced characteristic profile, acrylate polymers, mostly produced in solution, are used.

The advantage of this procedure is

a) to design the composition characteristics with regard to certain characteristic profiles via purposeful monomer compositions;

b) to establish desired molecular weights via the selection of suitable production parameters.

With regard to the question about readily volatile components, these compositions, however, exhibit clear disadvantages:

a) adhesive tapes produced with these compositions, as a rule, have solvent residues larger than 1 wt%, which, only over time, are released into the environment, unless an excellent drying was carried out. When using sensitive carriers or with thick composition layers, a 100% drying can almost be ruled out. Furthermore, with these compositions--in particular, if coated in thick layers--residue fractions of unreacted monomers are present with insufficient drying.

b) The polymers produced according to standardized polymerization methods have, moreover, broader molecular weight distributions. This leads to a result where the lower-molecular components tend to evaporate.

In US 5,681,654 ("Low fogging pressure-sensitive adhesive"), a low-fogging, self-adhesive tape is described. The use of a rubber composition is proposed as an adhesive, which uses a sulfur base as the

cross-linking system. In particular with cable bandaging, it also does not protect from interactions with the PVC wire insulation.

The adhesive tape is not free of fogging but rather is only low-fogging.

The goal of the invention is to create a free-fogging, self-adhesive tape, which does not have the disadvantages of the state of the art or does not have them to such an extent and which, nevertheless, is not limited in its usage capacity, in a manner similar to previously known products.

To attain this goal, the invention proposes a fogging-free self-adhesive tape, comprising a fogging-free carrier, on which, at least on one side, a fogging-free, pressure-sensitive adhesive composition is placed.

Preferably, fabrics, nonwovens, foils, paper, felts, foams, and coextrudates are used as carriers.

Furthermore, an adhesive composition based on acrylate hot melt with a K value of at least 20, in particular, greater than 30 (measured in 1 wt% solution in toluene, 25°C), obtainable by the concentration of a solution of such a composition to a system which can be processed as a hot melt, has proved to be advantageous.

The concentration can take place in correspondingly equipped boilers or extruders; in particular, a degassing extruder is preferred with an accompanying degassing.

Such an adhesive composition is described in German Patent Application DE 43 13 008. The solvent is completely removed, in an intermediate step, from the acrylate compositions produced in this way.

The K value is especially determined, thereby, in analogy to DIN 53 726.

In addition, other readily volatile components are thereby removed. After the coating from the melt, these compositions still have only slight fractions of volatile components. Thus all monomers/recipes claimed in the patent cited above can be used. Another advantage of the compositions described in the patent can be found in that they have a high K value and thus a high molecular weight. The specialist is

aware that systems with higher molecular weights can be crosslinked more efficiently. Thus, the fraction of volatile components drops correspondingly.

The solution of the composition can contain 5-80 wt%, in particular, 30-70 wt% solvent.

Also, single-screw, twin-screw, or multiscrew extruders with one or, in particular, two or more degassing units are preferably used.

In the adhesive composition based on acrylate hot melt, benzoin derivatives can be polymerized in, for example, benzoin acrylate or benzoin methacrylate, acrylic acid or methacrylic acid esters. Such benzoin derivatives are described in EP 0 578 151 A.

The adhesive composition can be based on UV-crosslinks. Other types of crosslinkings are also possible, for example the election crosslink.

In a particularly preferred embodiment, copolymers from (meth)acrylic acid and its esters with 1-25 C atoms, maleic, fumaric, and/or itaconic acid and/or their esters, substituted (meth)acrylamides, maleic acid anhydride, and other vinyl compounds, such as vinyl esters, in particular, vinyl acetate, vinyl alcohols, and/or vinyl ethers, are used as self-adhesive compositions.

The residual solvent content should be below 1 wt%.

It is particularly advantageous to use the self-adhesive tape, in accordance with the invention, for the sheathing of a bundle of cables; in addition, usage fields are, as a whole, preferably provided in automobile construction.

Also, the use of the self-adhesive tape as a carpet laying tape which adheres on both sides exhibits surprisingly good results.

Moreover, the inventive thought comprises self-adhesive tapes which are used [for] coating, as medical carriers--as carrier material for plasters or bandages.

Foils, for example made of polypropylene, polyethylene, polyester, fabrics made of cotton, viscose, viscose acetate, staple rayon, but also nonwovens made of viscose or polyester, and other mixtures, /4 prove to be suitable carrier materials for the production of medical products.

The self-adhesive tapes, in accordance with the invention, permit a large number of usage fields--thus, one- and two-sided adhesive tapes, carrier-less systems, plasters, and labels.

The self-adhesive tape coated on one side, in accordance with the invention, can be produced with particular preference according to a transfer method, as is disclosed in DE 43 24 748 C2. The adhesive composition is first placed on an intermediate carrier--a continuously circulating, antiadhesively equipped belt. From the belt, the layer of adhesive composition produced in such a manner is removed and bonded with the carrier material so that a one-sided adhesive tape is produced, which can be subsequently rolled to form a roll.

Such lower-molecular acrylate melt adhesive compositions, for example, with the name Acronal DS 3458, which as a result of the production process, have low K values, can be obtained from BASF.

As a result of the low K values, it was expected that the compositions have a high fraction of low-molecular components, which lead to evaporations. Accordingly, it was obvious to suspect that as a result of the difficult crosslinking capacity, not all polymer chains are bound into the matrix.

For the specialist it is very surprising that these compositions--when they are coated and crosslinked on fogging-free carriers--have good adhesive-technical characteristics and fogging values--thus, for example, with the production of carpet affixing or as adhesive tapes for the sheathing of bundles of cables.

The extremely low fraction of migrating components into the crosslinked composition systems (fogging values of ca. 100) represent an additional factor which has a positive influence on the aforementioned, described effect.

The adhesive tape, in accordance with the invention, will be described below with the aid of examples, without thereby wanting to unnecessarily limit the invention.

Example 1

On a nonwoven carrier (Maliwatt, 80 g/m^2, fineness 22, for example, from the Cottano Company), a UV-crosslinkable acrylate hot melt adhesive composition is applied, at a rate of 50 m/min, by rolling rod nozzle. Two different coating possibilities were thereby tested:

In the first process, 80 g/m^2 Acronal DS 3458 was applied in a direct line on the nonwoven. The temperature of the adhesive composition was 90°C to 110°C, and the coating tempered.

According to the second process variant, 50 g/m^2 Acronal 3458 was coated on a belt, and the adhesive composition was transferred to the nonwoven carrier, at 80°C and under a pressure of 8 bar, in a temperable bonding station. This variant permits a particularly comfortable control of the anchoring of the adhesive composition on the carrier material, avoiding an inadmissible composition puncture.

Both variants were crosslinked with UV rays at a further point in the system path (6 medium-pressure HG lamps at 120 W/cm). The degree of crosslinking could be adjusted variably via the UV dosage, so that it was possible to adjust the adhesive-technical characteristics (among others, adhesive power, rolling force) individually.

Both variants were wound, on a rod winder, to the desired lengths on rods and prepared to the desired widths, using an automatic cutting unit.

The adhesive-technical data of such an article were as follows:

Adhesive force on steel: 3.4 N/cm

Adhesive force on the back: 4.1 N/cm

Rolling force at 0.3 m/min: 2.6 N/cm

Maximum tension: 50.2 N/cm

HZK extension: 14.2%

The measurement of the adhesive forces was carried out by removing the adhesive tapes at a removal angle of 180° and a removal rate of 300 mm/min.

Fogging value:

according to Ford FLTM BO 116-03: 100%

according to Volvo STD1027, 2711: 100%

according to VW-PV 3015: 0.3 mg (theoretical (3 mg) < 3 mg).

The fogging value is thereby determined in the following manner:

A stipulated quantity of adhesive tape is exposed to a stipulated temperature, in a water bath, in a closed container, over a stipulated time period. On the glass plate with which the container is closed, a precipitate, which changes the light permeability of the glass plate, is deposited during this process.

Thus, a fogging value of 10 is equivalent to a light permeability of the glass plate which is now only 10%, and thus a poor fogging value. In contrast to this, a fogging value of 100 is to be designated, of course, as optimal, since measurable evaporations are not present and such an article is to be designated as free of fogging.

The fogging test is more and more required as a release criterion which the adhesive tape, in accordance with the invention, fulfills, in the automobile industry.

The adhesive tape thus produced is to be designated as a particularly stable adhesive tape for bundles of cables. The stability of the adhesive-technical data is also guaranteed after temperature storage.

In contrast to rubber adhesive compositions, there is no laking. Nor is there in interaction with the wire insulation material PVC.

Example 2

On a plaster foil carrier (polyolefin with an area-specific composition of 56 g/m^2), a /5
UV-crosslinkable acrylate hot melt adhesive composition is applied with a rolling rod nozzle, at a rate of 80 m/min.

38 g/m^2 of the UV-crosslinkable acrylate hot melt adhesive composition Acronal DS 3458 were applied on the foil with a rolling rod nozzle. The temperature of the adhesive composition was 145°C. A sufficient anchoring on the carrier was guaranteed by a tempering of the coating. The coated material was crosslinked by radiation with ultraviolet light from four medium-pressure Hg irradiators at 120 W/cm. Via the UV dosage, it was possible to variably adjust the degree of crosslinking, so that it was possible to individually adjust the corresponding adhesive characteristics (among others, adhesive force, rolling force).

The coated foil was bonded with a siliconized paper, wound to form a ball, and further processed into rolls.

The adhesive technical data of the coated foil were produced as follows:

Adhesive force on steel: 3.3 N/cm

Gel value (extraction with toluene): 50%.

Fogging value:

SAE J 1756 pt.6: 84 [Fogging No.] (= DIN 75 201 Process A)

SAE J 1756 pt.9 (= DIN 75 201 Process B): 0.2 [mg].

The fogging values is determined as described in Example 1.

This material also exhibits a good fogging value with a reduced crosslinking dosage. The material can be removed, once more, from the main area used for the bonding, without leaving behind residues.

Example 3

In the following table, two other embodiment examples of the adhesive tapes, in accordance with the invention, are indicated--carpet laying tapes.

Sample	4	6
Carrier	Polypropylene white, 50 µm	
Pretreatment	Primer	
Release paper	White release paper, 80 g/m^2	
Side covered with composition → Composition to the carpet	Acronal DS 3458	
Composition-open → Composition to the substrate	Substrates, such as parquet, PVC floors	Substrates, such as jointless floor
Coating speed	40 m/min	40 m/min
Radiation performance	720 Watt	720 Watt
Application weight	40 g/m^2	73 g/m^2
Adhesive force on steel		
	2.9 N/cm	4.3 N/cm

For the determination of the characteristics of the cemented adhesive tape upon detachment, it was cemented on PVC and stored in a drying cabinet at 40°C for three days.

The cemented sections were removed from the substrate at different removal angles and at different speeds (see table below).

	(1) Abzugswinkel											
	90°			180°			90°			180°		
(2) Abzugsgeschwindigkeit [cm/sec]	< 10	10	> 10	< 10	10	> 10	< 10	10	> 10	< 10	10	> 10
Note	1	1	3	1	1	1	1	1	1	1	1	1

Key: 1 Removal angle

2 Removal rate [cm/s]

The following code is valid for the notes listed: /6

Note	Composition residues in %*
1	No residues
2	< 10 (isolated composition points)
3	10 – 30
4	31 – 50
5	51 - 100

*: Relative to the total cementing area

The fogging-free, self-adhesive tapes described here exhibit only minimal to predominantly no composition residues according to the known methods, as is clear from the table above. In that fogging does not appear with the adhesive tapes, in accordance with the invention, it is possible to take up, once again, these self-adhesive tapes, largely without leaving residues, even from difficult substrates.

Claims

1. Fogging-free, self-adhesive tape, comprising a fogging-free carrier, on which, at least on one side, a fogging-free, pressure-sensitive adhesive composition is applied.

2. Self-adhesive tape according to Claim 1, characterized in that fabrics, nonwovens, foils, paper, felts, foams, and coextrudates are used as carriers.

3. Self-adhesive tape according to Claims 1 and 2, characterized in that, as the adhesive composition, one based on acrylate hot melt is used, which has a K value of at least 20, in particular, greater than 30.

4. Self-adhesive tape according to Claim 3, characterized in that the adhesive composition can be obtained by concentration a solution of such a composition to a system which can be processed as a hot melt.

5. Self-adhesive according to Claims 3 and 4, characterized in that the solution of the composition contains 5-80 wt%, in particular, 30-70 wt% solvent.

6. Self-adhesive tape according to Claims 3-5, characterized in that commercial solvents are used, in particular, low-boiling hydrocarbons, ketones, alcohols, and/or esters.

7. Self-adhesive tape according to Claims 3-6, characterized in that single-screw, twin-screw, or multiscrew extruders, with one or in particular, two or more degassing units, are used.

8. Self-adhesive tape according to Claims 3-7, characterized in that benzoin derivatives are polymerized into the adhesive composition on an acrylate hot melt basis.

9. Self-adhesive tape according to Claims 3-8, characterized in that the adhesive composition based on an acrylate hot melt is radiation-chemically cross-linked.

10. Self-adhesive tape according to Claims 3-9, characterized in that copolymers of (methy)acrylic acid and its esters, with 1-25 C atoms, maleic, fumaric, and/or itaconic acid and/or their esters, substituted (meth)acrylamides, maleic acid anhydride, and other vinyl compounds, such as vinyl esters, in particular, vinyl acetate, vinyl alcohols, and/or vinyl ethers, are used as self-adhesive compositions.

11. Self-adhesive tape according to Claims 3-10, characterized in that the residual solvent content is below 1 wt%.

12. Use of a self-adhesive tape according to at least one of the preceding claims for the sheathing of a bundle of cables.

13. Use of a self-adhesive tape according to one of the preceding claims, as a carpet laying tape, /7
adhesive on both sides.

14. Use of a self-adhesive tape according to one of the preceding claims, as a medical carrier.

15. Method for the production of a self-adhesive tape, coated on one side, according to one of the preceding claims, wherein the adhesive composition is first applied on an intermediate carrier, in particular, a continuously rotating, antiadhesively equipped belt; the layer of adhesive composition produced in such a manner is removed from the belt and is bonded with the carrier material.

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